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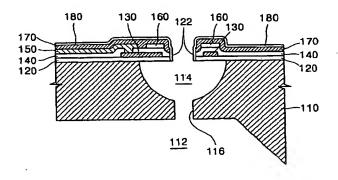
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## (54) Bubble-jet type ink-jet printhead and manufacturing method thereof

(57) A bubble-jet type ink-jet printhead and manufacturing method thereof are provided. The bubble-jet type ink-jet printhead includes a substrate (110) integrally having an ink supply manifold (112), an ink chamber (114), and an ink channel (116). A nozzle plate (120) having a nozzle (122) is stacked on the substrate. A heater (130) formed in an annular shape and centered around the nozzle and an electrode (150) for applying current to the heater are formed on the nozzle plate. An adiabatic layer (160) is formed on the heater for preventing heat generated by the heater from being conducted upward from the heater. Alternatively, a bubble-jet type ink-jet printhead may be formed on a silicon-on-insulator

(SOI) wafer having a first substrate, an oxide layer, and a second substrate stacked thereon. The first substrate integrally has a manifold, an ink chamber, and an ink channel. A nozzle is formed in the oxide layer and the second substrate. An adiabatic barrier is formed on the second substrate by limiting a portion of the second substrate in the shape of an annulus for forming an annular heater centered around the nozzle. In the bubble-jet type ink-jet printhead and manufacturing method thereof, the adiabatic layer or the adiabatic barrier is provided to transmit most of the heat generated by the heater to ink under the heater, thereby increasing energy efficiency.

### FIG. 5



#### Description

[0001] The present invention relates to an ink-jet printhead, and more particularly, to a bubble-jet type ink-jet printhead having a hemispherical ink chamber and a manufacturing method thereof.

[0002] Ink-jet printing heads are devices for printing a predetermined color image by ejecting small droplets of printing ink at desired positions on a recording sheet. Ink ejection mechanisms of an ink-jet printer are largely categorized into two types: an electro-thermal transducer type (bubble-jet type) in which a heat source is employed to form a bubble in ink causing ink droplets to be ejected, and an electro-mechanical transducer type in which a piezoelectric crystal bends to change the volume of ink causing ink droplets to be expelled.

[0003] FIG. 1A is an exploded perspective view showing an example of the structure of a conventional bubble-jet type ink-jet printhead disclosed in U. S. Patent No. 4,882,595, and FIG. 1B is a cross-section for explaining a process of ejecting ink droplets of the printhead of FIG. 1A. The conventional bubble-jet type inkjet printhead shown in FIGS. 1A and 1B includes a substrate 10, a barrier wall 12 disposed on the substrate 10 for forming an ink chamber 13 filled with ink 19, a heater 14 disposed in the ink chamber 13, and a nozzle plate 11 having a nozzle 16 for ejecting an ink droplet 19'. The ink 19 is introduced into the ink chamber 13 through an ink feed channel 15, and fills the nozzle 16 connected to the ink chamber 13 by capillary action. In the thusconfigured printhead, if current is supplied to the heater 14, the heater 14 generates heat to form a bubble 18 in the ink 19 within the ink chamber 13. The bubble 18 expands to exert pressure on the ink 19 present in the ink chamber 13, which causes an ink droplet 19' to be expelled through the nozzle 16. Then, the ink 19 is introduced through the ink feed channel 15 to refill the ink chamber 13.

[0004] Meanwhile, an ink-jet printhead having this bubble-jet type ink ejector needs to meet the following conditions. First, a simplified manufacturing process, low manufacturing cost, and high volume production must be allowed. Second, to produce high quality color images, creation of minute satellite droplets that trail ejected main droplets must be prevented. Third, when ink is ejected from one nozzle or ink refills an ink chamber after ink ejection, cross-talk with adjacent nozzles from which no ink is ejected must be prevented. To this end, a backflow of ink in the opposite direction of a nozzle must be avoided during ink ejection. Fourth, for high speed printing, a cycle beginning with ink ejection and ending with ink refill must be as short as possible. That is, an operating frequency must be high. Fifth, the printhead needs to have a small thermal load imposed due to heat generated by a heater and operate stably for a long period of time at high operating frequencies.

[0005] However, the above conditions tend to conflict with one another, and furthermore, the performance of

an ink-jet printhead is closely associated with structures of an ink chamber, an ink channel, and a heater, the type of formation and expansion of bubbles, and the relative size of each component.

[0006] In efforts to overcome problems related to the above requirements, ink-jet printheads having a variety of structures have been proposed in U. S. Patent Nos. 4,339,762; 5,760,804; 4,847,630; and 5,850,241 in addition to the above-referenced U. S. Patent No. 4,882,595, European Patent No. 317,171, and [Fan-Gang Tseng, Chang-Jin Kim, and Chih-Ming Ho, "A Novel Micoinjector with Virtual Chamber Neck", IEEE MEMS '98, pp. 57-62]. However, ink-jet printheads proposed in the above patents or literature may satisfy some of the aforementioned requirements but do not completely provide an improved ink-jet printing approach.

[0007] FIG. 2 shows a back-shooting type ink ejector of another example of a conventional bubble-jet type ink-jet printhead disclosed in IEEE MEMS '98, pp. 57-62. Here, a back-shooting technique refers to an ink ejection mechanism in which an ink droplet is ejected in a direction opposite to that in which a bubble expands. [0008] As shown in FIG. 2, in the back-shooting type printhead, a heater 24 is disposed around a nozzle 26 formed in a nozzle plate 21. The heater 24 is connected to an electrode (not shown) for applying current and is protected by a protective layer 27 of a predetermined material formed on the nozzle plate 21. The nozzle plate 21 is formed on a substrate 20 and an ink chamber 23 is formed for each nozzle 26 in the substrate 20. The ink chamber 23 is connected to an ink channel 25 and is filled with ink 29. The protective layer 27 for protecting the heater 24 is coated with an antiwetting layer 30, thereby repelling the ink 29. In the ink ejector configured as described above, if current is applied across the heater 24, the heater 24 generates heat to form a bubble 28 within the ink 29 filling the ink chamber 23. Then, the bubble 28 continues to expand by the heat supplied from the heater 24 and exerts pressure on the ink 29 within the ink chamber 23, thus causing the ink 29 near the nozzle 26 to be ejected through the nozzle 26 in the form of an ink droplet 29'. Then, the ink 29 is absorbed through the ink channel 25 to refill the ink chamber 23. [0009] However, the conventional back-shooting type ink-jet printhead has a problem in that a significant percentage of heat generated by the heater 24 is conducted and absorbed into portions other than the ink 29, such as the antiwetting layer 30 and the protective layer 27 near the nozzle 26. That is, it is desirable that the heat generated by the heater be used for boiling the ink 29 and forming the bubbles 28. However, a significant amount of heat is actually absorbed into other portions and the remainder of heat is used for forming the bubbles 28, thereby wasting energy supplied to form the bubble 28 and consequently degrading energy efficiency. This also increases the period from formation of the bubble 28 to collapse thereof. Thus, it is difficult to operate the ink jet printer head in high frequency.

[0010] Furthermore, the heat conducted to other portions significantly increases the temperature of the overall printhead as a print cycle runs thereby making long-time stable operation of the printhead difficult due to many thermal problems. For example, the heat produced by the heater is easily conducted to the surface near the nozzle 26 to excessively increase the temperature of that portion, thereby burning the antiwetting layer 30 near the nozzle 26 and changing the physical properties thereof.

[0011] To solve the above problems, it is a first object of the present invention to provide a bubble-jet type inkjet printhead with a structure that satisfies the above-mentioned requirements and has an adiabatic layer disposed around a heater so that energy supplied to the heater for bubble formation may be effectively used, and a manufacturing method thereof.

[0012] In order to achieve the above object, the present invention provides an embodiment of a bubble-jet type ink-jet printhead including: a substrate integrally having a manifold for supplying ink, an ink chamber filled with ink to be ejected, and an ink channel for supplying ink from the manifold to the ink chamber; a nozzle plate on the substrate, the nozzle plate having a nozzle through which ink is ejected at a location corresponding to a central portion of the ink chamber; a heater formed in an annular shape on the nozzle plate and centered around the nozzle of the nozzle plate; an electrode, electrically connected to the heater, for applying current to the heater; and an adiabatic layer formed on the heater for preventing heat generated by the heater from being conducted upward from the heater.

[0013] Preferably, the adiabatic layer is centered around the nozzle in the shape of annulus so as to cover the heater and the adiabatic layer is wider than the heater

[0014] Furthermore, the adiabatic layer may have a space filled with air or vacuum.

[0015] Due to the presence of the adiabatic layer, most of the heat generated by the heater is transferred down to ink, thereby increasing energy efficiency and operating frequency while allowing for long-time stable operation of the printhead.

[0016] The present invention also provides a method of manufacturing a bubble-jet type Ink-jet printhead including the steps of: forming a nozzle plate on a surface of a substrate; forming a heater having an annular shape on the nozzle plate; etching a bottom side of the substrate and forming a manifold for supplying ink; forming an electrode electrically connected to the heater on the nozzle plate; etching the nozzle plate and forming a nozzle having a diameter less than that of the heater on the inside of the heater; forming an adiabatic layer on the heater in the shape of an annulus; etching the substrate exposed by the nozzle and forming an ink chamber; and etching the substrate and forming an ink chamber.

[0017] The step of forming the adiabatic layer may include the steps of: forming an annular sacrificial layer on the heater; forming an annular slot on the sacrificial layer and exposing a portion of the sacrificial layer; and etching the sacrificial layer through the annular slot and forming the adiabatic layer having an interior space from which material has been removed.

[0018] Preferably, forming the adiabatic layer further includes the step of sealing the adiabatic layer by cogging up the annular slot with a predetermined material layer. The step of sealing the adiabatic layer is preferably performed by means of low pressure chemical vapor deposition (LPCVD) so that the adiabatic layer is kept substantially in a vacuum state.

[0019] According to the present invention, the substrate integrally has the ink chamber, the ink channel, and the ink supply manifold, and furthermore, the nozzle plate, the heater, and the adiabatic layer are integrally formed on the substrate, thereby allowing for a simple fabricating process and high volume production of printhead chips.

[0020] The present invention provides another embodiment of a bubble-jet type ink-jet printhead formed on a silicon-on-insulator (SOI) wafer including a first substrate, an oxide layer stacked on the first substrate, and a second substrate stacked on the oxide layer. The ink-jet printhead includes: a manifold for supplying ink, an ink chamber having a substantially hemispherical shape filled with ink to be ejected, and an ink channel for supplying ink from the manifold to the ink chamber, wherein the manifold, the ink chamber, and the ink channel are integrally formed on the first substrate; a nozzle, formed at a location of the oxide layer and the second substrate corresponding to a central portion of the ink chamber, for ejecting ink; an adiabatic barrier formed on the second substrate for forming an annular heater centered around the nozzle by limiting a portion of the second substrate in the form of an annulus; a heater protective layer stacked on the second substrate for protecting the heater; and an electrode, formed on the heater protective layer and electrically connected to the heater, for applying current to the heater

[0021] Preferably, the adiabatic barrier is formed along inner and outer circumferences so as to surround the heater, thereby insulating the heater from other portions of the second substrate. Preferably, the adiabatic barrier is formed in the shape of an annular groove and is sealed by the heater protective layer so that the nterior space thereof is kept in a vacuum state. Furthermore, the adiabatic barrier may be formed of predetermined insulating and adiabatic material.

[0022] The thus-configured bubble-jet type ink-jet printhead uses the adiabatic barrier to suppress the heat generated by the heater from being conducted to another portion, thereby increasing energy efficiency. Furthermore, the bubble-jet type ink-jet printhead provides for an ink ejector having a more robust structure on the SOI wafer.

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[0023] The present invention also provides a method of manufacturing a bubble-jet type ink-jet printhead using an SOI wafer. The manufacturing method includes the steps of: preparing the SOI wafer having a first substrate, an oxide layer stacked on the first substrate, and a second substrate stacked on the oxide layer; etching the second substrate and forming an adiabatic barrier having the shape of an annular groove limiting an annular heater; forming a heater protective layer on the second substrate for protecting the heater and sealing the adiabatic barrier; forming an electrode electrically connected to the heater on the heater protective layer; etching a bottom side of the first substrate and forming a manifold for supplying ink; sequentially etching the heater protective layer, the second substrate, and the oxide layer on the inside of the heater with a diameter less than that of the heater and forming a nozzle; etching the first substrate exposed by the nozzle and forming an ink chamber having a substantially hemispherical shape; and etching the first substrate and forming an ink channel for supplying ink from the manifold to the ink chamber.

[0024] Preferably, the adiabatic barrier is formed along inner and outer circumferences so as to surround the heater, thereby insulating the heater from another portion of the second substrate. Forming the heater protective layer is performed by means of LPCVD so that the adiabatic barrier is kept substantially in a vacuum state.

[0025] According to the present invention, components of the ink ejector are integrally formed on the SOI wafer, thereby allowing for a simple fabricating process and high volume production of printhead chips.

[0026] The above objects and advantages of the present invention will become more apparent by describing in detail preferred embodiments thereof with reference to the attached drawings in which:

FIG. 1A is an exploded perspective view showing an example of the structure of a conventional bubble-jet type ink-jet printhead, and FIG. 1B is a crosssection for explaining a process of ejecting ink droplets of the printhead of FIG. 1A;

FIG. 2 is a cross-section of an ink ejector of another example of a conventional bubble-jet type ink-jet printhead;

FIG. 3 is a schematic top view of an ink-jet printhead according to a first embodiment of the present invention;

FIG. 4 is an enlarged top view of the ink ejector of FIG. 3, and FIG. 5 is a cross-section of a vertical structure of the ink ejector taken along line A-A of FIG. 4;

FIG. 6 is a top view of a modified example of the ink ejector of FIG. 4;

FIG. 7 is a schematic top view of an ink-jet printhead according to a second embodiment of the present invention;

FIG. 8A is an enlarged top view of the ink ejector of FIG. 7, and FIGS. 8B-8D are cross-sections of vertical structures of the ink ejector respectively taken along lines B1-B1, B2-B2, and B3-B3;

FIG. 9 is a top view of a modified example of the ink ejector of FIG. 8A;

FIGS. 10A and 10B are cross-sections for explaining the ink ejection mechanism of the ink ejector of FIG. 4:

FIGS. 11-19 are cross-sections showing a process of manufacturing an ink-jet printhead having the ink ejector with the structure shown in FIGS. 4 and 5 according to a first embodiment of the present invention:

FIGS. 20-23 are cross-sections showing a process of manufacturing an ink-jet printhead having the ink ejector with the structure shown in FIGS. 8A-8D according to a second embodiment of the present invention;

FIG. 24 is a top view of an ink ejector of an ink-jet printhead according to a third embodiment of the present invention, and FIGS. 25A-25C are cross-sections of vertical structures of the ink ejector respectively taken along lines C1-C1, C2-C2, and C3-C3 of FIG. 24:

FIG. 26 is a top view of a modified example of the ink ejector of FIG. 24;

FIG. 27 is a top view of an ink ejector of an ink-jet printhead according to a fourth embodiment of the present invention, and FIG. 28 is a cross-section of a vertical structure of the ink ejector taken along line D-D of FIG. 27;

FIGS. 29A and 29B are cross-sections taken along lines C3-C3 of FIG. 24 for explaining the ink ejection mechanism of the ink ejector of FIG. 24;

FIGS. 30-36 are cross-sections showing a process of manufacturing an ink-jet printhead having the ink ejector with the structure shown in FIG. 24 according to a third embodiment of the present invention; and

FIGS. 37 and 38 are cross-sections showing a process of manufacturing an ink-jet printhead having the ink ejector with the structure shown in FIG. 27 according to a fourth embodiment of the present invention.

[0027] The present invention will now be described more fully with reference to the accompanying drawings, in which preferred embodiments of the invention are shown. This invention may, however, be embodied in many different forms and should not be construed as being limited to the embodiments set forth herein. Rather, these embodiments are provided so that this disclosure will be thorough and complete, and will fully convey the concept of the invention to those skilled in the art. In the drawings, the shapes and thicknesses of elements may be exaggerated for clarity, and the same reference numerals appearing in different drawings repre-

sent the same element. Further, it will be understood that when a layer is referred to as being "on" another layer or substrate, it can be directly on the other layer or substrate, or intervening layers may also be present. [0028] Referring to FIG. 3, in a printhead according to a first embodiment of the present invention, ink ejectors 100 are arranged on an ink supply manifold 112 shown with a dotted line in two rows in a staggered fashion. Bonding pads 20, to which wires are to be bonded, are electrically connected to each ink injector 100. Furthermore, the manifold 112 is connected to an ink container (now shown) for containing ink. Although the ink ejectors 100 are arranged in two rows as shown in FIG. 3, they may be arranged in one row. In order to achieve high resolution, the ink ejectors 100 may be arranged in three or more rows. The manifold 112 may be formed for each row of the ink ejectors 100. Furthermore, although the printhead using a single color of ink is shown in FIG. 2, three or four groups of ink ejectors may be disposed, one group for each color, for color printing.

[0029] FIG. 4 is an enlarged top view of the ink ejector 100 of FIG. 3, and FIG. 5 is a cross-section of a vertical structure of the ink ejector 100 taken along line A-A of FIG. 4. As shown in FIGS. 4 and 5, an ink chamber 114 filled with ink is formed on the surface of a substrate 110 of the ink ejector 100, the manifold 112 for supplying ink to the ink chamber 114 is formed on a bottom side of the substrate 110, and an ink channel 116 linking the ink chamber 114 and the manifold 112 is formed at a central bottom surface of the ink chamber 114. Here, the substrate 110 is preferably formed from silicon widely used in manufacturing integrated circuits. The ink chamber 114 preferably has a substantially hemispherical shape. Since the diameter of the ink channel 116 affects a backflow of ink being pushed back into the ink channel 116 during ink ejection and the speed at which ink refills after ink ejection, it needs to be finely controlled when forming the ink channel 116.

[0030] A nozzle plate 120 having a nozzle 122 is formed on the substrate 110 thereby forming an upper wall of the ink chamber 114. If the substrate 110 is formed of silicon, the nozzle plate 120 may be formed from an insulating layer such as a silicon oxide layer formed by oxidation of the silicon substrate 110 or a silicon nitride layer deposited on the substrate 110.

[0031] A heater 130 for bubble formation is formed on the nozzle plate 110 in an annular shape so that it is centered around the nozzle 122. The heater 130 consists of resistive heating elements such as polycrystalline silicon doped with impurities. A silicon nitride layer 140 may be formed on the nozzle plate 110 and the heater 130. Electrodes 150 are coupled to the heater 130 for applying pulse current.

[0032] An adiabatic layer 160 is provided on the heater 130 in an annular shape similar to that of the heater 130 with a silicon nitride layer 140 interposed therebetween. The adiabatic layer 160 serves to prevent heat generated by the heater 130 from being conducted up-

ward. To this end, the adiabatic layer 160 is preferably wider than the heater 130 so as to cover a large portion of the heater 130. The adiabatic layer 160 may be filled with air or kept in a vacuum state, which will be described below in greater detail.

[0033] A tetraetyleorthosilicate (TEOS) oxide layer 170 is formed on the silicon nitride layer 140, the electrode 150, and the adiabatic layer 160, and as described above, an antiwetting layer 180 is formed thereon in order to repel ink from the surface near the nozzle 122. [0034] FIG. 6 is a top view showing a modified example of the ink ejector of FIG. 4. A heater 130' is formed substantially in the shape of an omega, and one of the electrodes 150 is connected to each end of the heater 130'. That is, the two symmetrical annular parts of the heater 130 shown in FIG. 4 are coupled in parallel between the electrodes 140, whereas those of the omegashaped heater 130' shown in FIG. 6 are coupled in series therebetween.

[0035] FIG. 7 is a schematic top view of an ink-jet printhead according to a second embodiment of the present invention. Since this embodiment is very similar to the first embodiment, only the difference will now be described in brief.

[0036] Referring to FIG. 7, the printhead according to this embodiment includes ink ejectors 200 arranged in two rows in a staggered fashion along both sides of an ink supply manifold 212 shown with a dotted line, and bonding pads 202, to which wires are to be bonded, electrically connected to each ink ejector 200.

[0037] FIGS. 8A is an enlarged plan view of the ink ejector 200 of FIG. 7, and FIGS. 8B-8D are cross-sections showing vertical structures taken along lines B1-B1, B2-B2, and B3-B3 of FIG. 8A. Referring to FIGS. 8A-8D, each ink ejector 200 includes a substantially hemispherical ink chamber 214 filled with ink and an ink channel 216 formed shallower than the ink chamber 214 for supplying ink to the ink chamber 214, both of which are formed on a surface of a substrate 210. Also, the ink ejector 200 includes a manifold 212 connected with the ink channel 216 on a bottom surface thereof for supplying ink to the ink channel 216, and a stopper 218 formed at a point where the ink chamber 200 and the ink channel 220 meet each other for preventing a bubble from being pushed back into the ink channel 214 when the bubble expands.

[0038] A nozzle plate 220 having a nozzle 222 and a groove 224 for an ink channel are formed on the substrate 210, thereby forming an upper wall of the ink chamber 214. A heater 230 having an annular shape for forming a bubble and a silicon nitride layer 240 for protecting the heater 230 are formed on the nozzle plate 220. The heater 230 is connected to an electrode 250 formed of metal for applying pulse current. An adiabatic layer 260 is disposed on the heater 230. As described in the first embodiment, in order to prevent heat generated by the heater 230 from being conducted to above the heater 230, the adiabatic layer 260 is formed in an

annular shape similar to that of the heater 230, and is preferably wider than the heater 230 so as to cover a large portion of the heater 230. A TEOS oxide layer 270 is formed on the silicon nitride layer 240, the electrode 250, and the adiabatic layer 260, and an antiwetting layer 280 is formed thereon in order to repel ink from the surface near the nozzle 222.

[0039] FIG. 9 is a plan view of a modified example of the ink ejector 200 of FIG. 8A. Referring to FIG. 9, a heater 230' of an ink ejector 200' is formed substantially in the form of an omega, and an electrode 250 is coupled to each end of the heater 230'

[0040] The ink ejection mechanism of the ink ejector 100 shown in FIGS. 4 and 5 will now be described with reference to FIGS. 10A and 10B. First, referring to FIG. 10A, ink 190 is supplied to the ink chamber 140 through the manifold 112 and the ink channel 116 by capillary action. If a pulse current is applied to the heater 130 when the ink chamber 140 is filled with the ink 190, heat is generated by the heater 130. The heat is prevented from being conducted upward from the heater 130 by the adiabatic layer 160, thereby transmitting most heat to the ink 190 through the underlying nozzle plate 120. The transmitted heat boils the ink 190 to form bubbles 192. The bubbles 192 have an approximately doughnut shape conforming to the annular heater 130 as shown at the right side of FIG. 10A.

[0041] If the doughnut-shaped bubbles 192 expand with the lapse of time, as shown in FIG. 10B, the bubbles 192 coalesce below the nozzle 122 to form a substantially disk-shaped bubble 192', the center portion of which is concave. At the same time, the expanding bubble 192' causes an ink droplet 190' to be ejected from the ink chamber 114 through the nozzle 122. If the applied current cuts off, the heater 130 is cooled to shrink or collapse the bubble 192', and then the ink 190 refills the ink chamber 114.

[0042] In the ink ejection mechanism of the printhead according to this embodiment, the doughnut-shaped bubbles 192 coalesce under the central portion of the nozzle 122 to cut off the tail of the ejected ink droplet 190', thus preventing the formation of the satellite droplets. Furthermore, the area of the heater 130 having an annular or omega shape is so wide as to be rapidly heated and cooled, which quickens a cycle beginning with the formation of the bubble 192 or 192' and ending with the collapse thereof, thereby allowing for a quick response rate and high operating frequency. Furthermore, since the ink chamber 114 is hemispherical, a path along which the bubbles 192 and 192' expand is more stable as compared to a conventional ink chamber having the shape of a rectangular solid or a pyramid, and the formation and expansion of a bubble are quickly made thus ejecting ink within a relatively short time.

[0043] In particular, the adiabatic layer 160 formed on the heater 130 prevents heat generated by the heater 130 from being conducted upward from the heater 130 so that most of the heat is transmitted to the ink 190. Since the heat generated by the heater 130 is prevented from being conducted to the area above the heater 130 in this way, the temperature of the surface above the heater 130 is maintained low compared to that in a conventional printhead. Thus, as described above, the heat cannot burn the antiwetting layer 180 or change the physical properties thereof to lose hydrophobicity.

[0044] Furthermore, a greater amount of heat energy generated by the heater 130 is transferred to the ink 190, thereby increasing energy efficiency and ink operating frequency. That is, if the energy supplied to the heater 130 is fixed, the temperature of ink rises at high speed compared to that in a conventional printhead, thereby quickening a cycle beginning with the formation of the bubbles 192 and 192' and ending with the collapse and obtaining high operating frequency. If a predetermined operating frequency is to be obtained, the energy supplied to the heater 130 is reduced compared to that in a conventional printhead, thereby improving energy efficiency. Furthermore, the heat generated by the heater 130 is prevented from being conducted to a portion other than the ink 190, thereby preventing the temperature of the overall printhead from rising and thus enabling the printhead to be stably operated for a long time.

[0045] In addition, the expansion of the bubbles 192 and 192' is limited within the ink chamber 114, thereby preventing a backflow of the ink 190 and thus cross-talk between adjacent ink ejectors. Furthermore, it is very effective in preventing a backflow of the ink 190 if the diameter of the ink channel 116 is less than that of the nozzle 122.

[0046] A method of manufacturing an ink-jet printhead according to the present invention will now be described. FIGS. 11-19 are cross-sections taken along line A-A of FIG. 4 showing a method of manufacturing a printhead having the ink ejector shown in FIGS. 4 and 5 according to a first embodiment of the present invention.

[0047] Referring to FIG. 11, a silicon substrate having a crystal orientation of [100] and having a thickness of about 500 µm is used as a substrate 110 in this embodiment. This is because the use of a silicon wafer widely used in the manufacture of semiconductor devices allows for high volume production. Next, if the silicon wafer is wet or dry oxidized in an oxidation furnace, the top and bottom surfaces of the silicon substrate 110 are oxidized, thereby allowing silicon oxide layers 120 and 120' to grow. The silicon oxide layer 120 formed on the top surface of the substrate 110 will later be a nozzle plate where a nozzle is formed.

[0048] A very small portion of the silicon wafer is shown in FIG. 11, and tens to hundreds of printhead chips according to this invention are fabricated on a single wafer. Furthermore, as shown in FIG. 11, the silicon oxide layers 120 and 120' are developed on top and bottom surfaces of the substrate 110. This is because a batch type oxidation furnace having an oxidation atmosphere is used on the bottom surface of the silicon wafer

as well. However, if a single wafer type oxidation apparatus exposing only the top surface of a wafer is used, the silicon oxide layer 120' is not formed on the bottom surface of the substrate 110. For simplification, it will now be shown that a different material layer such a polycrystalline silicon layer, a silicon nitride layer and a tetraethyleorthosilicate (TEOS) oxide layer as will be described below is formed only on the top surface of the substrate 110.

[0049] Next, an annular heater 130 is formed on the silicon oxide layer 120 formed on the top surface of the substrate 110 by depositing polycrystalline silicon doped with impurities over the silicon oxide layer 120 and patterning this in the form of an annulus. Specifically, the polycrystalline silicon layer doped with impurities may be formed by low pressure chemical vapor deposition (LPCVD) using a source gas containing phosphorous (P) as impurities, in which the polycrystalline silicon is deposited to a thickness of about 0.7 - 1 µm. The thickness to which the polycrystalline silicon layer is deposited may be in different ranges so that the heater 120 may have appropriate resistance considering its width and length. The polycrystalline silicon layer deposited over the silicon oxide layer 120 is patterned by photolithography using a photomask and photoresist and an etching process using a photoresist pattern as an etch mask.

[0050] FIG. 12 shows a state in which a silicon nitride layer 140 has been deposited over the resulting structure of FIG. 11 and then a manifold 112 has been formed by etching the substrate 110 from its bottom surface. The silicon nitride layer 140 may be deposited to a thickness of about 0.5  $\mu\text{m}$  as a protective layer of the heater 130 using LPCVD. The manifold 112 is formed by obliquely etching the bottom surface of the wafer. More specifically, an etch mask that limits a region to be etched is formed on the bottom surface of the wafer, and wet etching is performed for a predetermined time using tetramethyl ammonium hydroxide (TMAH) as an etchant. Accordingly, etching in a crystal orientation of [111] is slower than etching in other orientations, thus forming the manifold 112 with a side surface inclined at 54.7 degrees. Although it has been described that the manifold 112 is formed by obliquely etching the bottom surface of the substrate 110, the manifold 112 may be formed by anisotropic etching.

[0051] FIG. 13 shows a state in which an electrode 150 has been formed. Specifically, a portion of the silicon nitride layer 140 at which the top of the heater 130 will be connected to the electrode 150 is etched to expose the heater 130. The electrode 150 is formed by depositing metal having good conductivity and patterning capability such as aluminum or aluminum alloy to a thickness of about 1 µm using a sputtering technique and patterning it. In this case, the metal layer of the electrode 150 is simultaneously patterned so as to form wiring lines (not shown) and the bonding pad (102 of FIG. 2) in other portions of the substrate 110.

[0052] FIG. 14 is a state in which a sacrificial layer 160' has been formed on the heater 130. The sacrificial layer 160' is formed by depositing polycrystalline silicon to a thickness of about 1  $\mu m$  on the silicon nitride layer 140 overlying the heater 130 and patterning it in the form of an annulus. Specifically, the polycrystalline silicon may be deposited by means of LPCVD, and its width is preferably greater than that of the heater 130. The sacrificial layer 160' becomes an adiabatic layer for preventing heat generated by the heater 130 from being conducted above the heater 130.

[0053] Then, as shown in FIG. 15, a TEOS oxide layer 170 is deposited over the substrate 110. The TEOS oxide layer 170 is formed by CVD, in which the TEOS oxide layer 170 may be deposited to a thickness of about 1 µm at low temperature where the electrode 150 and the bonding pad made from aluminum or aluminum alloy are not transformed, for example, at no greater than 400°C. [0054] Next, as shown in FIG. 16, photoresist is applied over the substrate 110 and patterned to form a photoresist pattern PR. The photoresist pattern PR exposes a portion of the TEOS oxide layer 170 at which a nozzle 122 is to be formed and a portion of the TEOS oxide layer 170 on top of the sacrificial layer 160' in the form of an annulus. Using the photoresist pattern PR as an etch mask, the TEOS oxide layer 170, the silicon nitride layer 140, and the silicon oxide layer 120 are sequentially etched to form the nozzle 122 having a diameter of about 16-20 μm, and the TEOS oxide layer 170 on top of the sacrificial layer 160' is etched to form an annular slot 162 having a width of about 1 \( \mu m \). Although it has been described that the nozzle 122 is formed by sequentially etching the TEOS oxide layer 170, the silicon nitride layer 140, and the silicon oxide layer 120, it may be formed by etching the silicon nitride layer 140 and the silicon oxide layer 120 in the step shown in FIG. 13.

[0055] FIG. 17 shows a state in which the substrate 110 and the sacrificial layer 160' exposed by the photoresist pattern PR are etched to form an ink chamber 114, an ink channel 116, and an adiabatic layer 160. First, the ink chamber 114 may be formed by isotropically etching the substrate 110 using the photoresist pattern PR as an etch mask. More specifically, the substrate 110 is dry etched for a predetermined period of time using XeF2 gas or BrF3 gas as an etch gas. Then, as shown in FIG. 17, the substantially hemispherical ink chamber 114 is formed with depth and radius of about 20 µm. At the same time, the sacrificial layer (160' of FIG. 15) is etched through the annular slot 162 to form the adiabatic layer 160 having an interior space from which the material layer, i.e., the polycrystalline silicon layer, has been removed. The ink chamber 114 and the adiabatic layer 160 may be simultaneously or sequentially formed.

[0056] The ink chamber 114 may be formed by anisotropically etching the substrate 110 using the photoresist pattern PR as an etch mask and then isotropically etch-

ing it. That is, the silicon substrate 110 may be anisotropically etched by means of inductively coupled plasma etching or reactive ion etching using the photoresist pattern PR as an etch mask to form a hole (not shown) having a predetermined depth. Then, the silicon substrate 110 is isotropically etched in the manner described above. Alternatively, the ink chamber 114 may be formed by changing a part of the substrate 110 in which the ink chamber 114 is to be formed into a porous silicon layer and selectively etching and removing the porous silicon layer.

[0057] Subsequently, the substrate 110 is anisotropically etched using the photoresist pattern PR as an etch mask to form the ink channel 116 linking the ink chamber 114 and the manifold 112 at the bottom of the ink chamber 114. The anisotropic etching may be performed by inductively coupled plasma etching or reactive ion etching as described above.

[0058] FIG. 18 shows a state in which the photoresist pattern PR is removed by ashing and strip from the resulting structure shown in FIG. 17. The antiwetting layer (180 of FIG. 5) may be applied over the uppermost surface in this state, thereby completing the printhead according to this embodiment. Since the adiabatic layer 160 is exposed to the outside through the annular slot 162 in the state shown in FIG. 18, ink or foreign material tends to break into the adiabatic layer 160 through the annular slot 162, thereby degrading the adiabatic efficiency thereof. Thus, as shown in FIG. 19, it is preferable that the annular slot 162 is clogged up before forming the antiwetting layer.

[0059] FIG. 19 shows a state in which the annular slot 162 has been clogged up by a silicon nitride layer 175 formed on the TEOS oxide layer 170 around the annular slot 162. The silicon nitride layer 175 is formed by depositing silicon nitride to a thickness of about 0.5-1  $\mu m$ by CVD and patterning the same. The thickness to which the silicon nitride layer 175 is deposited varies depending on the width of the annular slot 162. That is, the silicon nitride layer 175 is sufficiently thick to clog up the annular slot 162. For example, if the width of the annular slot 162 is about 1 µm, the thickness of the silicon nitride layer 175 is 0.5 μm or greater. The silicon nitride layer 175 may be replaced with an oxide layer or may be formed over the entire surface of the TEOS oxide layer 170. In this case, the adiabatic layer 160 is a sealed air adiabatic layer filled with only air. If the silicon nitride layer 175 is deposited by LPCVD, the adiabatic layer 160 is a vacuum adiabatic layer which is kept actually in a vacuum state.

[0060] FIGS. 20-23 are cross-sections taken along line B3-B3 of FIG. 8A showing a process for manufacturing an ink-jet printhead having an ink ejector with the structure shown in FIGS. 8A-8D according to a second embodiment of the present invention. The manufacturing method according to the second embodiment of this invention is similar to the first embodiment except for the step of forming an ink channel. That is, the second em-

bodiment is the same as the first embodiment up to the step of forming the TEOS oxide fover 170 shown in FIG. 15. Both embodiments are different in the subsequent step for forming an ink channel. Thus, the method of manufacturing the printhead having the ink ejector shown in FIG. 8A according to the second embodiment of the present invention will now be described with respect to the difference.

[0061] As shown in FIG. 20, a TEOS oxide layer 270 is formed and patterned to form a groove 224 for an ink channel on the outside of a heater 230 in a straight line up to the area above a manifold 212. The groove 224 may be formed by sequentially etching the TEOS oxide layer 270, a silicon nitride layer 240, and a silicon oxide layer 220. Also, the groove 224 has a length of about 50  $\Phi$ m and a width of about 2  $\Phi$ m.

[0062] Then, as shown in FIG. 21, photoresist Is applied over a substrate 210 and patterned to form the photoresist pattern PR. The photoresist pattern PR exposes a portion of the TEOS oxide layer 270 at which a nozzle 222 is to be formed and a portion of the TEOS oxide layer 270 on top of a sacrificial layer 260' in the form of an annulus. Then, using the photoresist pattern PR as an etch mask, the TEOS oxide layer 270, the silicon nitride layer 240, and the silicon oxide layer 220 are sequentially etched to form the nozzle 222 having a diameter of about 16-20  $\mu$ m, and the TEOS oxide layer 270 on top of the sacrificial layer 260' is etched to form an annular slot 262 having a width of about 1  $\mu$ m.

[0063] FIG. 22 shows a state in which the substrate 210 and the sacrificial layer 260' exposed by the photoresist pattern PR are etched to form an ink chamber 214, an ink channel 216, and an adiabatic layer 260. First, the ink chamber 114 may be formed by isotropically etching the substrate 210 using the photoresist pattern PR as an etch mask. More specifically, the substrate 210 is dry etched for a predetermined period of time using XeF2 gas or BrF3 gas as an etch gas. Then, as shown in FIG. 22, the substantially hemispherical ink chamber 214 is formed with depth and radius of about 20 μm, and the ink channel 216 for linking the ink chamber 214 with the manifold 212 is formed with depth and radius of about 8 μm. Also, a projecting stopper 218 is formed by etching at the point where the ink chamber 214 and the ink channel 216 meet each other. At the same time, the sacrificial layer (260' of FIG. 20) is etched through the annular slot 262 to form the adiabatic layer 260 having an interior space from which the material layer, i.e., the polycrystalline silicon layer, has been removed. The ink chamber 214, the ink channel 216, and the adiabatic layer 260 may be simultaneously or sequentially formed.

[0064] FIG. 23 shows a state in which the photoresist pattern PR is removed from the resulting structure shown in FIG. 17 by ashing and stripping. The antiwetting layer (280 of FIG. 8D) may be applied over the uppermost surface in this state to complete the printhead according to this embodiment. However, as in the first

embodiment, it is preferable that the annular slot 262 is clogged up before coating the antiwetting layer in order to close the adiabatic layer 260. The step is the same as the counterpart in the first embodiment, and a detailed explanation thereof will be omitted.

[0065] FIG. 24 is an enlarged top view of an ink-jet printhead according to a third embodiment of the present invention, and FIGS. 25A-25C are cross-sections of the vertical structures of the ink ejector taken along lines C1-C1, C2-C2, and C3-C3 of FIG. 24, respectively.

[0066] Referring to FIGS. 24 and 25A-25C, an ink ejector 300 of the ink-jet printhead according to this embodiment is configured in the way shown in FIG. 7 basically using the stacked structure of a silicon-on-insulator (SOI) wafer 310. The SOI wafer 310 typically has a structure in which a first substrate 311, an oxide layer 312 formed on the first substrate 311, and a second substrate 313 bonded to the oxide layer 312 are stacked. The first substrate 311 is formed of monocrystalline silicon and has a thickness of several hundreds of micrometers. The oxide layer 312 is formed by oxidizing the surface of the first substrate 311 and has a thickness of about 1  $\mu m$ . The second substrate 313 is typically formed of monocrystalline silicon and has a thickness of about several tens of micrometers, for example, 20  $\mu m$ .

[0067] An ink chamber 324 filled with ink, which has a substantially hemispherical shape, and an ink channel 326 formed shallower than the ink chamber 324 for supplying ink to the ink chamber 324 are formed on the top surface of the first substrate 311 of the SOI wafer 310. A manifold 322 connected with the ink channel 326 for supplying ink to the ink channel 326 is formed on the bottom surface of the first substrate 311. A stopper 329 is formed at the point where the ink chamber 324 and the ink channel 326 meet each other for preventing an expanding bubble from being pushed back into the ink channel 326.

[0068] The oxide layer 312 and the second substrate 313 of the SOI wafer 310 form an upper wall of the ink chamber 324 formed on the surface of the substrate 311 as described above. Since the upper wall of the ink chamber 324 has a thickness of about 20  $\mu$ m due to the thickness of the second substrate 313, the ink chamber 324 and the ink ejector 300 are more robust.

[0069] A nozzle 330, through which an ink droplet is ejected, is formed at a location in the oxide layer 312 and the second substrate 313 of the SOI wafer 310 corresponding to a central portion of the ink chamber 324. A groove 328 for an ink channel is formed at a location corresponding to a central line extending in a longitudinal direction of the ink channel 326.

[0070] An annular heater 340 centered around the nozzle 330 for forming a bubble is formed at a portion of the second substrate 313 of the SOI wafer 310. The heater 340 has inner and outer circumferences surrounded by an adiabatic barrier 342 formed in the shape

of an annular groove with a width of about 1-2 μm, thereby insulating the heater 340 from other portions of the ink ejector. That is, the heater 340 is formed by limiting the portion of the second substrate 313 on top of the ink chamber 324 surrounded by the adiabatic barrier 342. The adiabatic barrier 342 not only insulates the heater 340 from other portions of the second substrate 313 but also prevents heat generated by the heater 340 from being conducted to other elements through the second substrate 313. The adiabatic barrier 342 may be filled with air but is preferably kept in a vacuum state. Alternatively, predetermined insulating and adiabatic material fills the interior adiabatic barrier 342 to form the adiabatic barrier 342 formed of the predetermined insulating and adiabatic material.

[0071] A heater protective layer 350 is formed on the second substrate 313 on which the heater 340 has been formed. The heater protective layer 350 not only protects the heater 340 but also seals the adiabatic barrier 342. In this case, the interior space of the adiabatic barrier 342 is preferably kept in vacuum as described above. An electrode 360 is connected to the heater 340 for applying pulse current.

[0072] FIG. 26 is a top view showing a modified example of the ink ejector of FIG. 24. Referring to FIG. 26, a heater 340' of an ink ejector 300' is formed substantially in the shape of an omega, and one of two electrodes 360 is connected to each end of the heater 340'. That is, the heater 340 shown in FIG. 24 is coupled in parallel between the electrodes 360, whereas the heater 340' shown in FIG. 26 is coupled in series therebetween. An adiabatic barrier 342' surrounding the heater 340' has an omega shape conforming to the shape of the heater 340'. The shapes and configurations of other components of the ink ejector 300' such as the ink chamber 324, the ink channel 326, the nozzle 330, and the groove 328 for an ink channel are the same as those of their counterparts in the ink ejector 300 shown in FIG. 24.

[0073] FIG. 27 is a top view of an ink ejector of an inkjet printhead according to a fourth embodiment of the present invention, and FIG. 28 is a cross-section of a vertical structure of the ink ejector taken along line D-D of FIG. 27.

[0074] Referring to FIGS. 27 and 28, an ink ejector 400 according to this embodiment is configured in a way shown in FIG. 3 and formed on an SOI wafer 410. an ink chamber 424 having a substantially hemispherical shape in which ink is filled is formed on the top surface of a first substrate 411 of the SOI wafer 410. A manifold 422 for supplying ink to the ink chamber 424 is formed on the bottom surface of the first substrate 411 so that the manifold 422 is located below the ink chamber 424. An ink channel 426 linking the ink chamber 424 and the manifold 422 is formed at the center of the bottom of the ink channel 426 affects a backflow of ink being pushed back into the ink channel 426 during ink ejection and the

speed at which ink refills the ink chamber 424 after ink ejection, it needs to be finely controlled when forming the ink channel 426.

[0075] A nozzle 430 is formed in an oxide layer 412 and a second substrate 413 of the SOI wafer 410, and a heater 440 surrounded by an adiabatic barrier 442 is formed at a portion of the second substrate 413. A heater protective layer 450 is deposited over the second substrate 413 on which the heater 440 has been formed, and an electrode 460 is coupled to the heater 440.

[0076] Although the heater 440 has an annular shape in this embodiment, it may be formed in the shape of an omega as shown in FIG. 26.

[0077] The ink ejection mechanism of an ink-jet printhead having the ink ejector of FIG. 24 according to the present invention will now be described with reference to FIGS. 29A and 29B.

[0078] Referring to FIG. 29A, ink 380 is supplied to the ink chamber 324 through the manifold 322 and the ink channel 326 by capillary action. If pulse current is applied across the heater 340 when the ink 380 fills the ink chamber 324, the heater 340 generates heat. The generated heat is prevented from being conducted to the sides of the heater 340 by the adiabatic barrier 342, thus transferring most of the heat to the ink 380 through the underlying oxide layer 312. This boils the ink 380 to form bubbles 391. The bubbles 391 have a substantially doughnut shape conforming to the shape of the heater 340 as shown at the right side of FIG. 29A.

[0079] If the doughnut-shaped bubbles 391 expand with the lapse of time, as shown in FIG. 29B, the bubbles 391 coalesce below the nozzle 22 to form a substantially disk-shaped bubble 392, the central portion of which is concave. At the same time, the expanding bubble 392 causes an ink droplet 380' to be ejected from the ink chamber 324 through the nozzle 330. If the applied current cuts off, the heater 340 is cooled to shrink or collapse the bubble 392, and then the ink 380 refills the ink chamber 324.

[0080] In the ink ejection mechanism of the printhead according to this embodiment, the doughnut-shaped bubbles 391 coalesce under the central portion of the nozzle 330 to form the disk-shaped bubble 392. This cuts off the tail of the ejected ink droplet 380', thus preventing the formation of the satellite droplets. Furthermore, since the ink chamber 324 has a hemispherical shape, a path along which the bubbles 391 and 392 expand is more stable than in a conventional ink chamber having the shape of a rectangular solid or a pyramid, and the formation and expansion of a bubble occur quickly thus ejecting ink within a relatively short time. Furthermore, the area of the heater 340 having an annular or omega shape is wide enabling it to be rapidly heated and cooled, which quickens a cycle beginning with the formation of the bubble 391 or 392 and ending with the collapse thereof, thereby allowing for a quick response rate and high operating frequency.

[0081] Furthermore, the expansion of the bubble 391

and 392 is limited to within the ink chamber 324, thereby preventing a backflow of the ink 380 and thus cross-talk between adjacent ink ejectors. Furthermore, since the ink channel 326 is shallower than the ink chamber 324 and the stopper 329 is formed at a point where the ink chamber 324 and the ink channel 326 meet each other, it is effective in preventing the ink 380 and the bubble 392 from being pushed back into the ink channel 316.

[0082] In particular, heat generated by the heater 340 is prevented from being conducted to portions other than the ink 380 by the adiabatic barrier 342, thereby transmitting a greater amount of heat energy generated by the heater 340 to the ink 380. This increases effective use of energy to decrease a time taken from the formation of the bubbles 391 and 392 until the collapse thereof, thereby providing a high operating frequency.

[0083] Furthermore, the upper wall of the ink chamber 324 formed by the oxide layer 312 and the second substrate 313 of the SOI wafer 310 is sufficiently thick to prevent transformation of the ink chamber 324 and the upper wall thereof due to heat generated by the heater 340 and a pressure change resulting from expansion and collapse of the bubbles 391 and 392 within the ink chamber 324. Thus, this constantly maintains the shape of the bubbles 391 and 392 formed in the ink chamber 324, makes the ejection of the ink droplet 380' uniform, and increases the durability of the ink ejector 300.

[0084] In addition, the nozzle 330 formed in the oxide layer 312 and the second substrate 313 of the SOI wafer 310 is sufficiently long to accurately guide a direction in which the ink droplet 380' is ejected without a separate guide.

[0085] Amethod of manufacturing an ink-jet printhead according to the present invention using an SOI wafer will now be described. FIGS. 30-36 are cross-sections showing a method of manufacturing a printhead having the ink ejector of FIG. 24 according to a third embodiment of the present invention. The left and right sides of FIGS. 30-36 are cross-sections taken along lines C1-C1 and C3-C3 of FIG. 24, respectively.

[0086] Referring to FIG. 30, an SOI wafer 310 is prepared. As described above, the SOI wafer 310 has a structure in which a first substrate 311, an oxide layer 312, and a second substrate 313 are stacked. The SOI wafer 310 having the structure as described above is easily available from wafer manufacturers. In this case, the SOI wafer 310 has an approximately 10-30 µm thick and preferably about 20 µm thick second substrate 313. [0087] Then, as shown in FIG. 31, the second substrate 313 of the SOI wafer 310 is etched to form an adiabatic barrier 342 having a width of about 1-2 µm in the shape of an annular groove. The adiabatic barrier 342 surrounds the inner and outer circumferences of a heater 340 so that the annular heater 340 limited by the adiabatic barrier 342 is insulated from other portions of the second substrate 313.

[0088] FIG. 32 shows a state in which a heater protective layer 350 and an electrode 360 have been

formed on the second substrate 313 having the heater 340 and the adiabatic barrier 342. The heater protective layer 350 is formed by depositing a TEOS oxide layer on the second substrate 313 to a thickness of about  $0.5\text{-}1~\mu\text{m}$  by means of CVD. Although the TEOS oxide layer is used as the heater protective layer 350 in this embodiment, an oxide layer formed of another material or a nitride layer may be used instead. The heater protective layer 350 is preferably deposited using low temperature CVD since the interior space of the adiabatic barrier 342 can be kept in a vacuum state. Before forming the heater protective layer 350, the adiabatic barrier 342 may be filled with predetermined insulating and adiabatic material to form the adiabatic barrier 342 made of the predetermined insulating and adiabatic material. [0089] Subsequently, a portion of the heater protective layer 350 at which the top of the heater 130 is to be connected to the electrode 360 is etched to expose the heater 340. The electrode 360 is formed by depositing metal having good conductivity and patterning capability such as aluminum or aluminum alloy to a thickness of about 1  $\mu m$  using a sputtering technique and patterning the same. In this case, the metal layer of the electrode 360 is simultaneously patterned so as to form wiring lines and the bonding pad at other portions of the second substrate 313.

[0090] FIG. 33 shows a state in which the first substrate 311 has been etched from its bottom surface to form a manifold 322. The manifold 322 is formed by obliquely etching the bottom surface of the first substrate 311. More specifically, an etch mask that limits a region to be etched is formed on the bottom surface of the first substrate 311, and wet etching is performed for a predetermined time using tetramethyl ammonium hydroxide (TMAH) as an etchant. Accordingly, etching in a crystal orientation of [111] is slower than etching in other orientations to form the manifold 322 with a side surface inclined at 54.7 degrees. The manifold 322 may be formed prior to forming the electrode 360. Although it has been described that the manifold 322 is formed by obliquely etching the bottom surface of the first substrate 311, the manifold 112 may be formed by anisotropic etching.

[0091] FIG. 34 shows a state in which the TEOS oxide layer 370 has been deposited after forming a nozzle 330 and a groove 328 for an Ink channel. The nozzle 330 is formed by anisotropically etching the heater protective layer 350, the second substrate 313, and the oxide layer 312 in sequence until the first substrate 311 is exposed on the inside of the heater 340 with a diameter less than that of the heater 340, for example, 16-20  $\mu$ m. The groove 328 for an ink channel is formed by sequentially etching the heater protective layer 350, and the second substrate 313 and the oxide layer 312 of the SOI wafer 310 in a straight line from the outside of the heater 340 to the area above the manifold 322. The groove 328 for an ink channel has a length of about 50  $\mu$ m and a width of about 2  $\mu$ m. Also, the groove 328 for an ink channel

may be formed in the step shown in FIG. 35.

[0092] Then, the TEOS oxide layer 370 is formed. The TEOS oxide layer 370 may be deposited by means of CVD to a thickness of about 1  $\mu$ m at low temperature at which the electrode 360 and the bonding pad made from aluminum or aluminum alloy are not transformed, for example, at no greater than 400°C.

[0093] Then, as shown in FIG. 35, the TEOS oxide layer 370 on the bottom surfaces of the nozzle 322 and groove 328 for an ink channel is etched to expose the first substrate 311.

[0094] FIG. 36 shows a state in which the exposed first substrate 311 has been etched to form the ink chamber 324 and the ink channel 326. The ink chamber 324 may be formed by isotropically etching the first substrate 311 exposed through the nozzle 330. Specifically, the first substrate 311 is dry etched for a predetermined period of time using XeF<sub>2</sub> gas or BrF<sub>3</sub> gas as an etch gas. Then, as shown in FIG. 36, the substantially hemispherical ink chamber 324 is formed with depth and radius of about 20  $\mu m$ , and the ink channel 326 for linking the ink chamber 324 and the manifold 322 is formed with depth and radius of about 8-12 µm. Also, a projecting stopper 329 is formed by etching at the point where the ink chamber 324 and the ink channel 326 meet each other. The ink chamber 324 and the ink channel 326 may be simultaneously or sequentially formed. The ink chamber 324 may be formed by anisotropically etching the surface of the first substrate 311 to a predetermined depth and then isotropically etching the same. In this way, the ink-jet printhead according to the third embodiment of the present invention is completed.

[0095] FIGS. 37 and 38 are cross-sections taken along line D-D of FIG. 27 showing a method of manufacturing an ink-jet printhead having the ink ejector with the structure as shown in FIG. 27 according to a fourth embodiment of the present invention.

[0096] A method of manufacturing the ink-jet printhead according to this embodiment is the same as the manufacturing method according to the third embodiment shown in FIGS. 30-36 except for the step of forming the manifold and the ink channel. This embodiment is the same as the third embodiment up to the fabricating steps shown in FIGS. 30-32 but is different in the position where the manifold is formed in the step shown in FIG. 33. That is, a manifold 422 in this embodiment is formed by etching the bottom surface of a first substrate 411 so that the manifold 422 is positioned at the bottom of an ink chamber to be subsequently formed.

[0097] This embodiment is also the same as the third embodiment in the steps shown in FIGS. 34-36 except for the formation of an ink channel. In this embodiment, as shown in FIG. 38, the middle portion of the bottom of an ink chamber 424 is anisotropically etched to form an ink channel 426 connected with the manifold 422, thereby completing the ink-jet printhead according to the fourth embodiment of the present invention shown in FIG. 27.

[0098] As described above, a bubble-jet type ink-jet printhead according to the present invention and manufacturing method thereof according to the present invention have several advantages. First, an adiabatic layer or an adiabatic barrier surrounded by a heater prevents heat generated by the heater from being conducted to an area above the heater or to portions other than ink, so that most of the heat flows into the ink below the heater, thereby allowing for a high operating frequency and stable operation for a long time while increasing energy efficiency. Second, the bubble is doughnut-shaped and the ink chamber is hemispherical, thereby preventing a backflow of ink and thus cross-talk between adjacent ink ejectors while preventing the formation of satellite droplets. Third, the upper wall of an ink chamber formed by an oxide layer and a second substrate of an SOI wafer is sufficiently thick and robust to prevent transformation of the ink chamber and the upper wall thereof due to heat generated by a heater and a pressure change within the ink chamber. Thus, this constantly maintains the shape of the bubbles 391 and 392 formed in the ink chamber 324, makes the ejection of an ink droplet uniform, and increases the durability of the entire ink ejector. Fourth, according to a conventional printhead manufacturing method, a nozzle plate, an ink chamber, and an ink channel are manufactured separately and bonded to each other. However, a method of manufacturing a printhead according to this invention involves forming the nozzle plate and the annular heater integrally with the substrate having the manifold, the ink chamber and the ink channel thereon, thereby simplifying the fabricating process and preventing occurrences of mis-alignment. Thus, the manufacturing method according to this invention is compatible with a typical manufacturing process for a semiconductor device, thereby facilitating high volume production. In particular, the steps of forming an oxide layer on the substrate as a nozzle plate and of depositing a heater of a predetermined material may be omitted when using the SOI wafer, thereby simplifying the fabrication process.

[0099] Although this invention has been described with reference to preferred embodiments thereof, it will be understood by those skilled in the art that various changes in form and details may be made therein. For example, materials forming elements of a printhead according to this invention may not be limited to those described herein. That is, the substrate 100 may be formed of a material having good processibility, other than silicon, and the same is true of a heater, an electrode, a silicon oxide layer, or a nitride layer. Furthermore, the stacking and formation method for each material are only examples, and a variety of deposition and etching techniques may be adopted.

[0100] Also, the sequence of process steps in a method of manufacturing a printhead according to this invention may differ. For example, specific numeric values illustrated in each step may vary within a range in which the manufactured printhead can operate normally.

[0101] The shape of the ink chamber, the ink channel, and the heater in the printhead according to this invention provides a high response rate and high operating frequency. Furthermore, doughnut-shaped bubbles coalesce at the center, which prevents the formation of satellite droplets.

[0102] This invention makes it easier to control a backflow of ink and operating frequency by controlling the diameter of the ink channel. Furthermore, the ink channer, the ink channel, and the manifold are arranged vertically to reduce the area occupied by the manifold on a plane, thereby increasing the integration density of a printhead.

#### Claims

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1. A bubble-jet type ink-jet printhead comprising:

a substrate (110) integrally having a manifold (112) for supplying ink, an ink chamber (114) filled with ink to be ejected, and an ink channel (116) for supplying ink from the manifold (112) to the ink chamber (114);

a nozzle plate (120) on the substrate (110), the nozzle plate having a nozzle (122) through which ink is ejected at a location corresponding to a central portion of the ink chamber (114); a heater (130) formed in an annular shape on the nozzle plate and centered around the nozzle (122) of the nozzle plate (120);

an electrode (150), electrically connected to the heater (130), for applying current to the heater; and

an adiabatic layer (160) formed on the heater (130) for preventing heat generated by the heater from being conducted upward from the heater

- 2. The bubble-jet type ink-jet printhead as claimed in claim 1, wherein the manifold (112) is formed on a bottom side of the substrate (110) and the ink channel (116) is formed at the bottom of the ink chamber (114) so that it connects with the manifold.
  - 3. The bubble-jet type ink-jet printhead as claimed in claim 1, wherein the manifold (112) is formed on a bottom side of the substrate (110) and the ink channel (116) is formed on the surface of the substrate (110) to a predetermined depth so that the ink channel is connected to the manifold and the ink chamber.
    - The bubble-jet type ink-jet printhead as claimed in any of claims 1 to 3, wherein the ink chamber (114) has a substantially hemispherical shape.
    - 5. The bubble-jet type ink-jet printhead as claimed in

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any of claims 1 to 4, wherein the adiabatic layer (160) is centered around the nozzle (122) in the shape of an annulus so as to cover the heater (130).

- The bubble-jet type ink-jet printhead as claimed in any of claims 1 to 5, wherein the adiabatic layer (160) is wider than the heater(130).
- 7. The bubble-jet type ink-jet printhead as claimed in any of claims 1 to 6, wherein the adiabatic layer (160) has a space filled with air.
- The bubble-jet type ink-jet printhead as claimed in any of claims 1 to 6, wherein the adiabatic layer (160) has a space maintained in a state of vacuum.
- A method of manufacturing a bubble-jet type ink-jet printhead, the method comprising the steps of:

forming a nozzle plate (120) on a surface of a substrate (110); forming a heater (130) having an annular shape on the nozzle plate (120); etching a bottom side of the substrate (110) and forming a manifold (112) for supplying ink; forming an electrode (150) electrically connected to the heater (130) on the nozzle plate (120); etching the nozzle plate (120) and forming a nozzle (122) having a diameter less than that of the heater on the inside of the heater; forming an adiabatic layer (160) on the heater in the shape of an annulus; etching the substrate (110) exposed by the nozzle and forming an ink chamber (114); and etching the substrate (110) and forming an ink channel (116) for supplying ink from the (112) manifold to the ink chamber (114).

10. The method as claimed in claim 9, wherein forming the adiabatic layer (160) comprises the steps of:

forming an annular sacrificial layer (160') on the heater (130); forming an annular slot (162) on the sacrificial layer (160') and exposing a portion of the sacrificial layer; and etching the sacrificial layer (160') through the annular slot (162) and forming the adiabatic layer (160) having an interior space from which material has been removed.

- 11. The method as claimed in claim 10, wherein forming the adiabatic layer (160) further comprises the step of sealing the adiabatic layer by cogging up the annular slot (162) with a predetermined material layer.
- The method as claimed in claim 11, wherein sealing the adiabatic layer (160) is performed by means of

low pressure chemical vapor deposition so that the adiabatic layer is kept substantially in a vacuum state.

- The method as claimed in claim 11, wherein the predetermined material layer is a silicon nitride layer.
  - 14. The method as claimed in any of claims 10 to 13, wherein the sacrificial layer (160') is formed of polycrystalline silicon.
  - 15. The method as claimed in any of claims 10 to 14, wherein etching the sacrificial layer (160') is performed simultaneously with forming the ink chamber (114).
  - 16. The method as claimed in any of claims 9 to 15, wherein in forming the ink chamber (114), the substrate (110) exposed by the nozzle is (122) isotropically etched to form the ink chamber having a substantially hemispherical shape.
  - 17. The method as claimed in any of claims 9 to 16, wherein in forming the ink channel (116), the substrate at the bottom of the ink chamber (114) is anisotropically etched with a predetermined diameter to form the ink channel connecting with the manifold (112).
- 18. The method as claimed in any of claims 9 to 16, wherein forming the ink channel (116) comprises the steps of:

etching the nozzle plate (220) from the outside of the heater (230) toward the manifold (212) and forming a groove (224) for an ink channel which exposes the substrate (210); and isotropically etching the substrate (210) exposed by the groove for an ink channel (216).

19. A bubble-jet type ink-jet printhead formed on a silicon-on-insulator (SOI) wafer (310) having a first substrate (311), an oxide layer (312) stacked on the first substrate, and a second substrate (313) stacked on the oxide layer, the bubble-jet type inkjet printhead comprising:

a manifold (322) for supplying ink, an ink chamber (324) having a substantially hemispherical shape filled with ink to be ejected, and an ink channel (326) for supplying ink from the manifold to the ink chamber, wherein the manifold (322), the ink chamber (324), and the ink channel (326) are integrally formed on the first substrate (311);

a nozzle (330), formed at a location of the oxide layer (312) and the second substrate (313) corresponding to a central portion of the ink cham-

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ber (324), for ejecting ink;

an adiabatic barrier (342) formed on the second substrate (313) for forming an annular heater (340) centered around the nozzle by limiting a portion of the second substrate in the form of an annulus:

a heater protective layer (350) stacked on the second substrate (313) for protecting the heater (340); and

an electrode (360), formed on the heater protective layer and electrically connected to the heater (340), for applying current to the heater.

- 20. The bubble-jet type ink-jet printhead as claimed in claim 19, wherein the adiabatic barrier (342) is formed along inner and outer circumferences so as to surround the heater (340), thereby insulating the heater from other portions of the second substrate (313).
- 21. The bubble-jet type ink-jet printhead as claimed in claim 20, wherein the adiabatic barrier (342) is formed in the shape of an annular groove and is sealed by the heater protective layer (350) so that the interior space thereof is kept in a vacuum state.
- The bubble-jet type ink-jet printhead as claimed in claim 20, wherein the adiabatic barrier (342) is formed of predetermined insulating and adiabatic material.
- 23. The bubble-jet type ink-jet printhead as claimed in any of claims 19 to 22, wherein the ink channel (326) is formed on the surface of the first substrate (311) to a predetermined depth so that both ends thereof are connected to the manifold (322) and the ink chamber (324).
- 24. The bubble-jet type ink-jet printhead as claimed in any of claims 19 to 22, wherein the ink channel (326) is formed at the bottom of the ink chamber (324) so as to connect with the manifold (322).
- 25. A method of manufacturing a bubble-jet type ink-jet printhead using a silicon-on-insulator (SOI) wafer (310), the method comprising the steps of:

preparing the SOI wafer (310) having a first substrate (311), an oxide layer (312) stacked on the first substrate, and a second substrate (313) stacked on the oxide layer;

etching the second substrate (313) and forming an adiabatic barrier (342) having the shape of an annular groove limiting an annular heater (340);

forming a heater protective layer (350) on the second substrate for protecting the heater and sealing the adiabatic barrier;

forming an electrode (360) electrically connected to the heater on the heater protective layer; etching a bottom side of the first substrate (311) and forming a manifold (322) for supplying ink; sequentially etching the heater protective layer (350), the second substrate (313) and the oxide layer (312) on the inside of the heater with a diameter less than that of the heater and forming a nozzle (330);

etching the first substrate (311) exposed by the nozzle (330) and forming an ink chamber (324) having a substantially hemispherical shape; and

etching the first substrate (311) and forming an ink channel (326) for supplying ink from the manifold (322) to the ink chamber (324).

- 26. The method as claimed in claim 25, wherein the thickness of the second substrate (313) of the SOI wafer is 10-30 μm.
- 27. The method as claimed in claim 25 or 26, wherein the adiabatic barrier (342) is formed along inner and outer circumferences so as to surround the heater (340), thereby insulating the heater from another portion of the second substrate (313).
- 28. The method as claimed in any of claims 25 to 27, wherein forming the heater protective layer (350) is performed by means of low pressure chemical vapor deposition so that the adiabatic barrier (342) is kept substantially in a vacuum state.
- 29. The method as claimed in claim 27, prior to forming the heater protective layer (350), further comprising the step of filling the adiabatic barrier (342) with predetermined insulating and adiabatic material.
- 30. The method as claimed in any of claims 25 to 29, wherein forming the ink channel (316) comprises the steps of:

sequentially etching the heater protective layer (350), the second substrate (313), and the oxide layer (312) from the outside of the heater (340) toward the manifold (322) and forming a groove (328) for an ink channel (316) that exposes the first substrate; and isotropically etching the first substrate (311) exposed by the groove for an ink channel.

31. The method as claimed in any of claims 25 to 29, wherein in forming the ink channel (316), the first substrate (311) at the bottom of the ink chamber is anisotropically etched with a predetermined diameter to form the ink channel connected with the manifold (322).

## FIG. 1A (PRIOR ART)

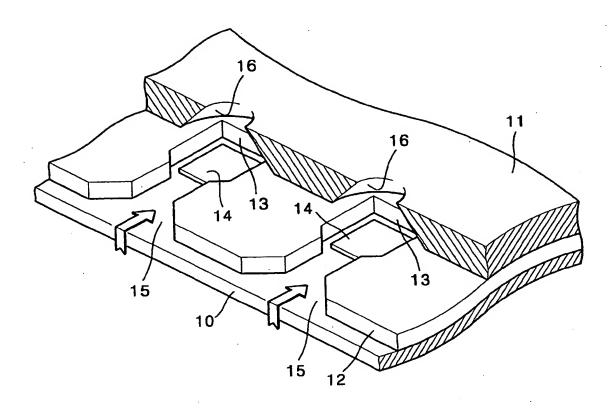
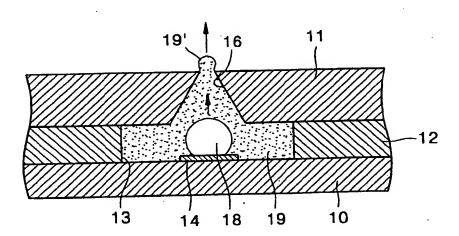


FIG. 1B (PRIOR ART)



## FIG. 2 (PRIOR ART)

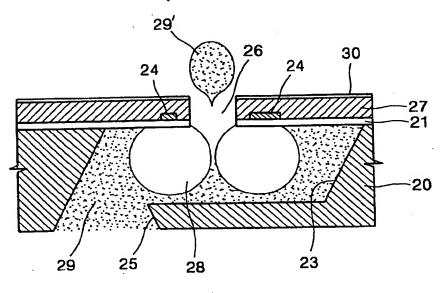


FIG. 3

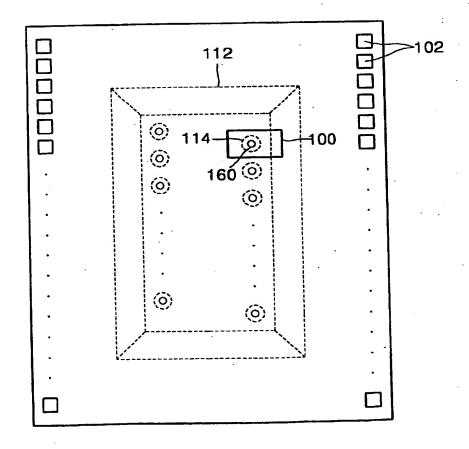


FIG. 4

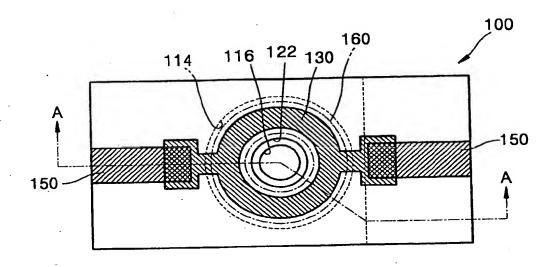


FIG. 5

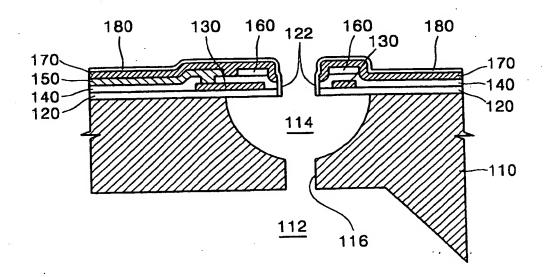


FIG. 6

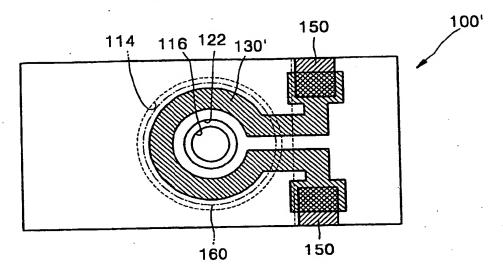


FIG. 7

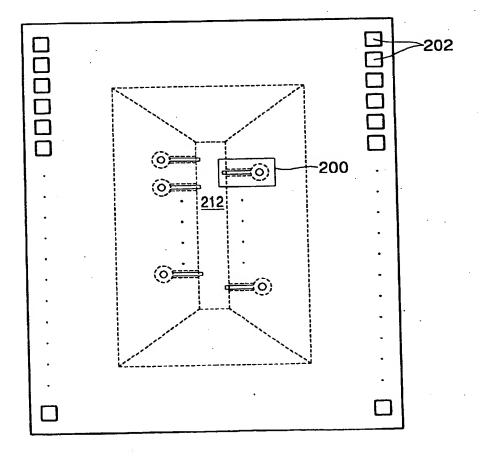


FIG. 8A

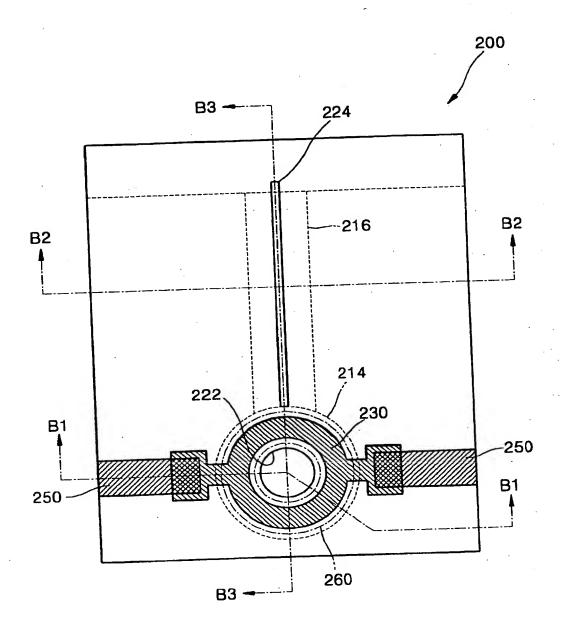


FIG. 8B

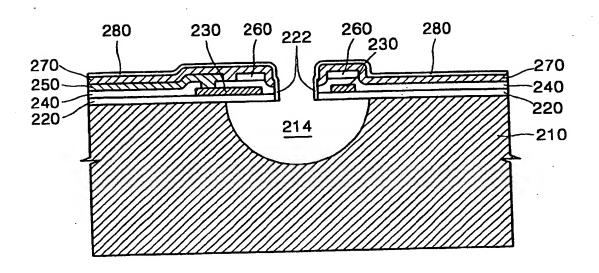
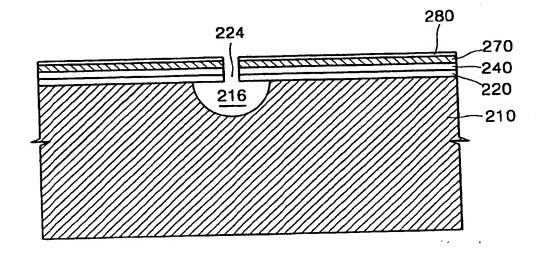
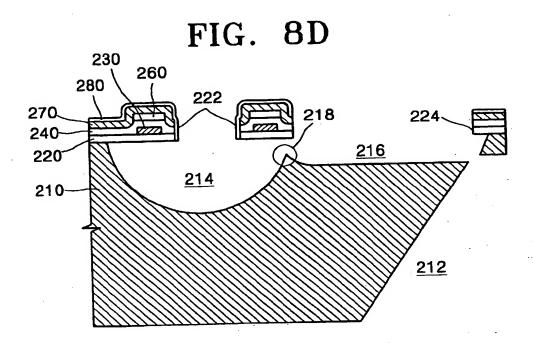
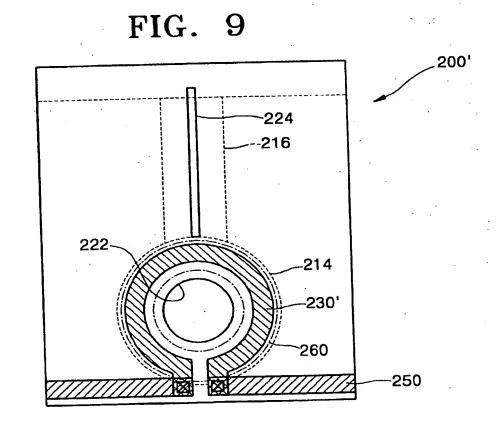


FIG. 8C







## FIG. 10A

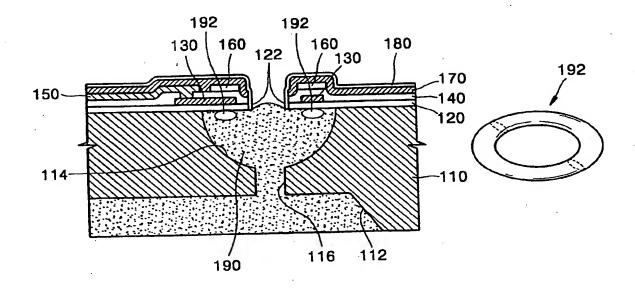


FIG. 10B

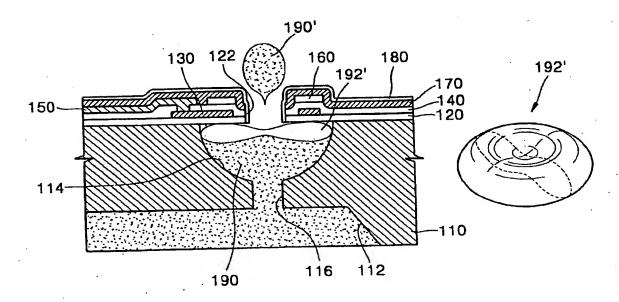


FIG. 11

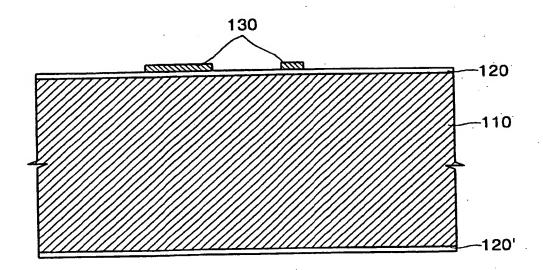


FIG. 12

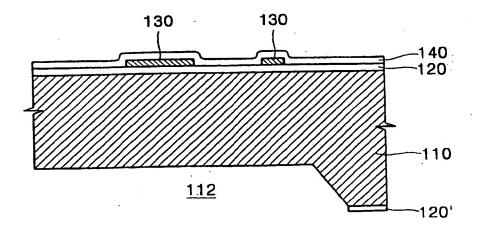


FIG. 13

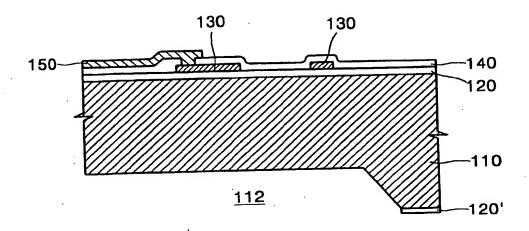


FIG. 14

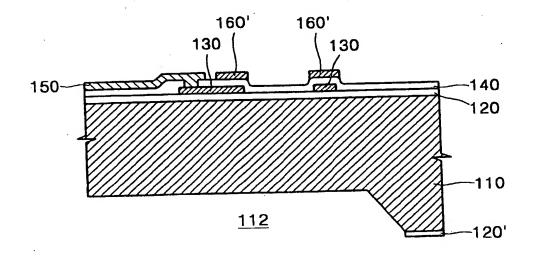


FIG. 15

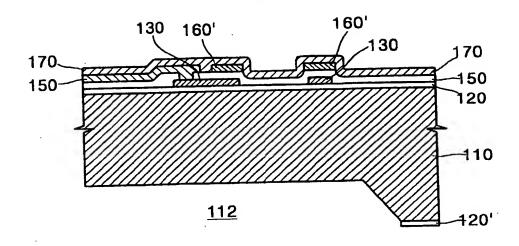


FIG. 16

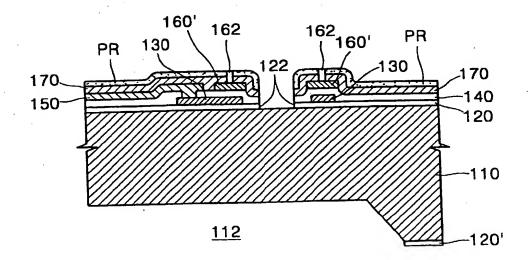


FIG. 17

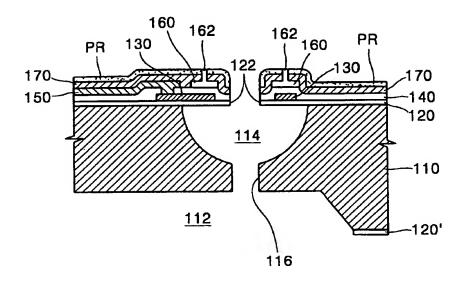


FIG. 18

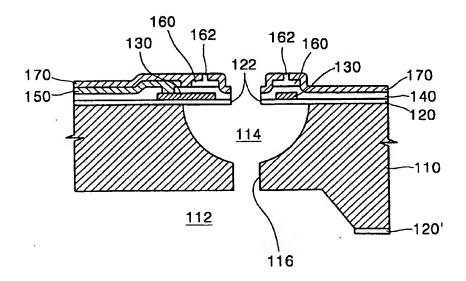


FIG. 19

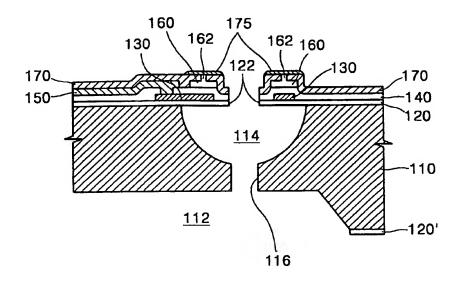
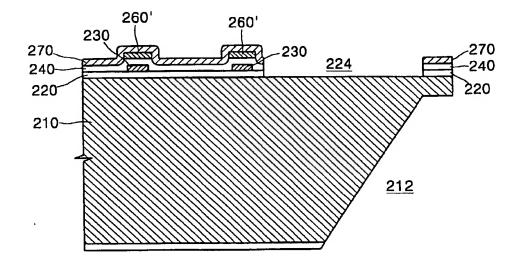


FIG. 20



## FIG. 21

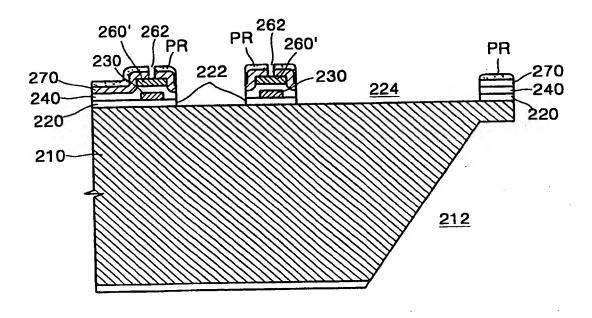


FIG. 22

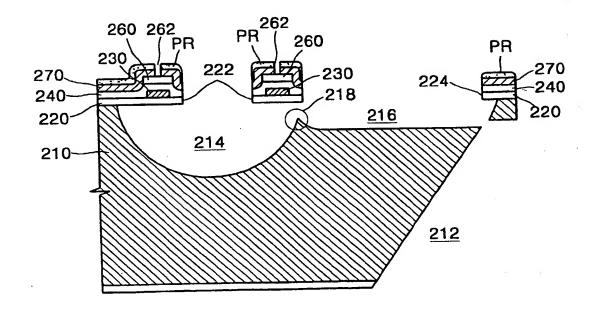


FIG. 23

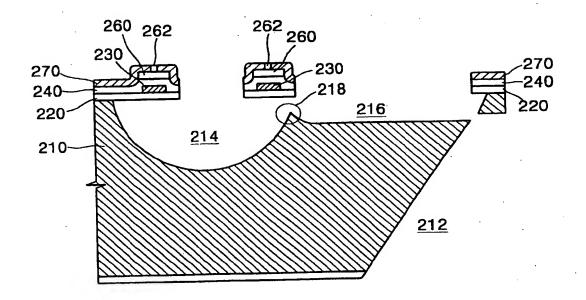


FIG. 24

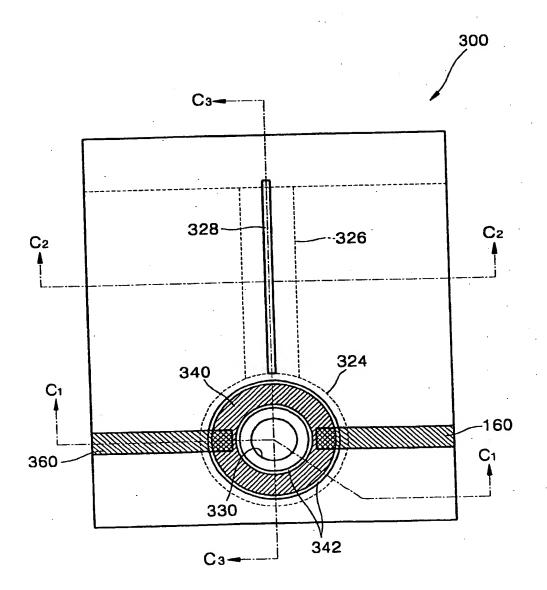


FIG. 25A

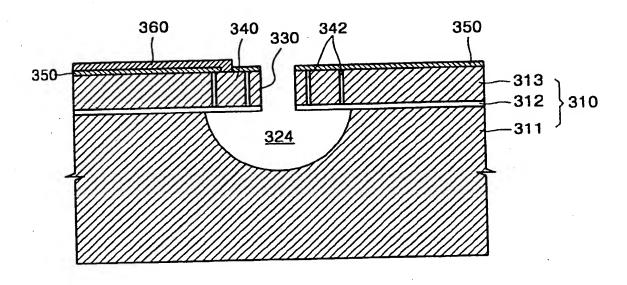


FIG. 25B

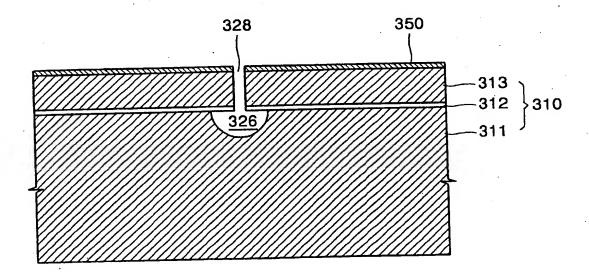


FIG. 25C

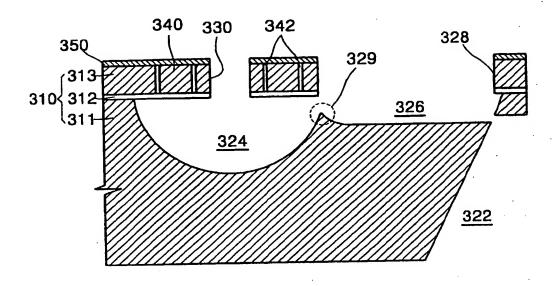


FIG. 26

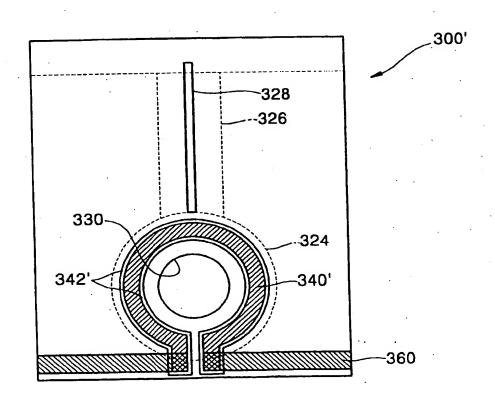


FIG. 27

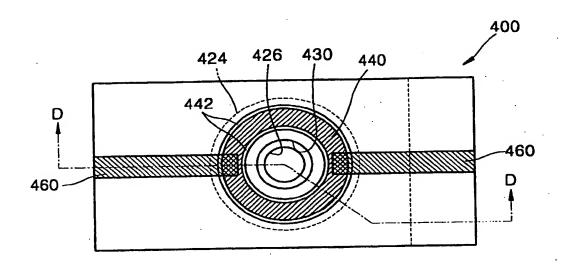
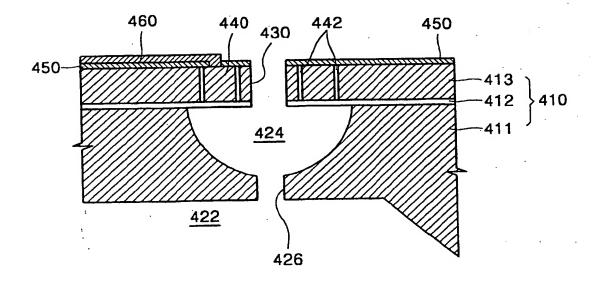


FIG. 28



## FIG. 29A

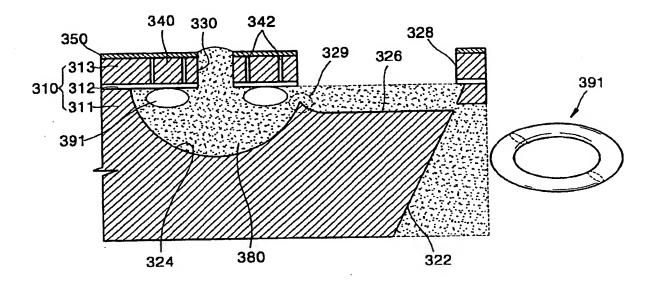


FIG. 29B

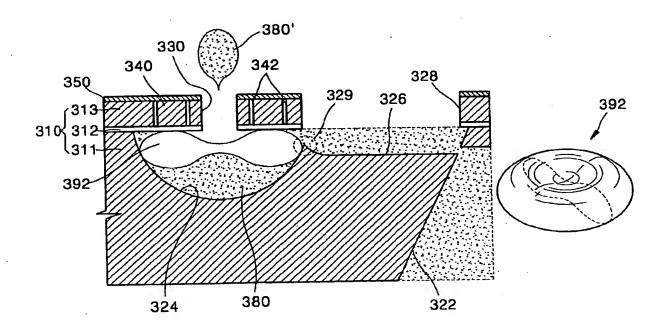


FIG. 30

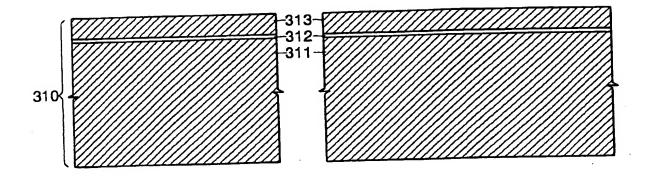


FIG. 31

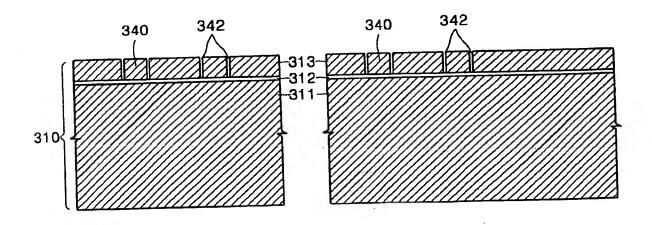


FIG. 32

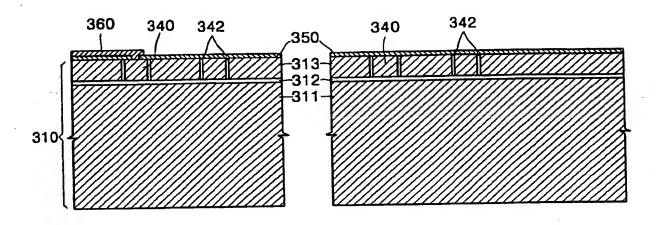


FIG. 33

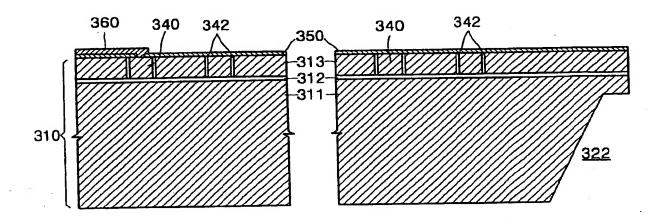


FIG. 34

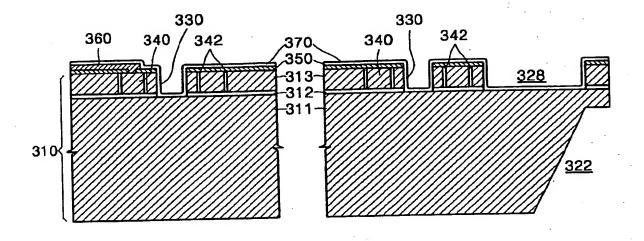


FIG. 35

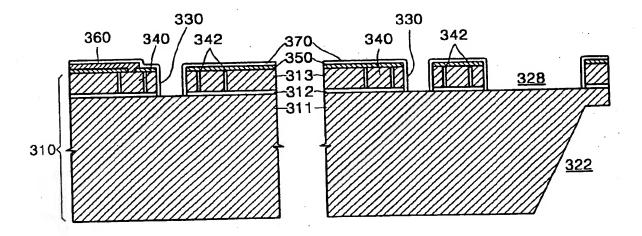


FIG. 36

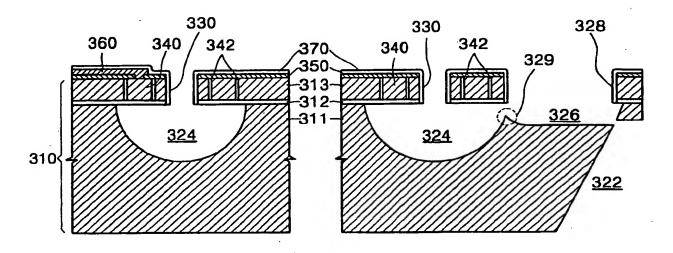


FIG. 37

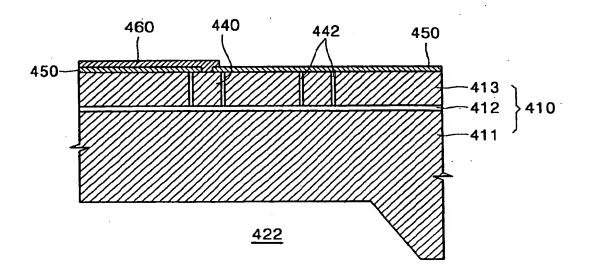
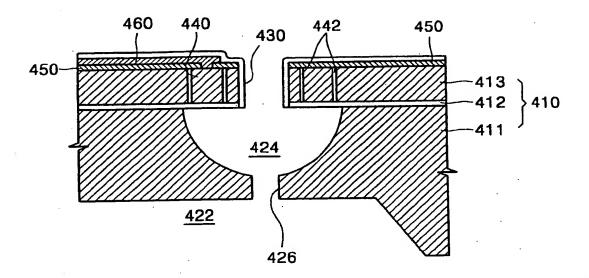


FIG. 38





# Europäisches Patentamt European Patent Office Office européen des brevets



(11) EP 1 215 048 A3

(12)

## **EUROPEAN PATENT APPLICATION**

(88) Date of publication A3: 12.03.2003 Bulletin 2003/11

(51) Int Cl.7: **B41J 2/14**, B41J 2/16

(43) Date of publication A2: 19.06.2002 Bulletin 2002/25

(21) Application number: 01310427.8

(22) Date of filing: 13.12.2001

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MC NL PT SE TR
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(30) Priority: 15.12.2000 KR 2000077167 19.01.2001 KR 2001003161

(71) Applicant: SAMSUNG ELECTRONICS Co. Ltd. Kyungki-do, Seoul (KR)

(72) Inventors:

• Maeng, Doo-jin

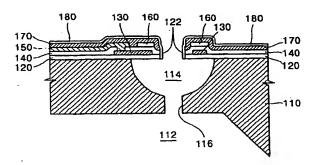
Mapo-qu, Seoul (KR)

- Kuk, Keon Yongin-City, Kyungki-do (KR)
- Oh, Yong-soo Seongnam-city, Kyungki-do (KR)
- Kim, Hyeon-cheol Seochu-gu (KR)
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  Elkington and Fife
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  8 Pembroke Road
  Sevenoaks, Kent TN13 1XR (GB)

(54) Bubble-jet type ink-jet printhead and manufacturing method thereof

A bubble-jet type ink-jet printhead and manu-(57)facturing method thereof are provided. The bubble-jet type ink-jet printhead includes a substrate (110) integrally having an ink supply manifold (112), an ink chamber (114), and an ink channel (116). A nozzle plate (120) having a nozzle (122) is stacked on the substrate. A heater (130) formed in an annular shape and centered around the nozzle and an electrode (150) for applying current to the heater are formed on the nozzle plate. An adiabatic layer (160) is formed on the heater for preventing heat generated by the heater from being conducted upward from the heater. Alternatively, a bubble-jet type ink-jet printhead may be formed on a silicon-on-insulator (SOI) wafer having a first substrate, an oxide layer, and a second substrate stacked thereon. The first substrate integrally has a manifold, an ink chamber, and an ink channel. A nozzle is formed in the oxide layer and the second substrate. An adiabatic barrier is formed on the second substrate by limiting a portion of the second substrate in the shape of an annulus for forming an annular heater centered around the nozzle. In the bubble-jet type ink-jet printhead and manufacturing method thereof, the adiabatic layer or the adiabatic barrier is provided to transmit most of the heat generated by the heater to ink under the heater, thereby increasing energy efficienсу.







#### **EUROPEAN SEARCH REPORT**

EP 01 31 0427

ategory	Citation of document with indication	TO BE RELEVANT	Relevant	CLASSIFICATION OF THE
aleguly	of relevant passages		to claim	APPLICATION (Int.CI.7)
X	US 6 019 457 A (SILVERBI 1 February 2000 (2000-02	ROOK KIA) 2-01)	1-6,9, 16-20, 22-24, 27-31	B41J2/14 B41J2/16
A	* column 8, line 36 - 1 * column 19, line 1 - 1	ine 65 * ine 14 *	10,21	
Ä	US 5 861 902 A (BEERLING 19 January 1999 (1999-0 * column 12, line 10	1-19)	9-18	
X	WO 96 32274 A (SILVERBR KODAK CO (US)) 17 October 1996 (1996-1		1-6,9, 17,19, 20, 22-25, 27-31	
Α	* page 66, line 15 - li	ne 18; figures 1,9	10,21	
	* page 14, line 12 - li * page 58, line 21 - pa	ne 31 * ge 66, line 14 *		
		-		TECHNICAL FIELDS SEARCHED (Int.CL7)
				B41J
	: #1			
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! 				
	The present search report has been d	rawn up for all claims		1
	Place of search	Date of completion of the search		Examiner
	MUNICH	15 January 2003	Ac	chermann, D
X:pa Y:pa	CATEGORY OF CITED DOCUMENTS  articularly relevant if taken alone articularly relevant if combined with another roument of the same category	T : theory or princi E : earlier patent d after the tilling d D : document cited L : document cited	ocument, but put ate I in the applicatio	blished on, or In



**Application Number** 

EP 01 31 0427

CLAIMS INCURRING FEES							
The present European patent application comprised at the time of filing more than ten claims.							
Only part of the claims have been paid within the prescribed time limit. The present European search report has been drawn up for the first ten claims and for those claims for which claims fees have been paid, namely claim(s):							
No claims fees have been paid within the prescribed time limit. The present European search report has been drawn up for the first ten claims.							
LACK OF UNITY OF INVENTION							
The Search Division considers that the present European patent application does not comply with the requirements of unity of invention and relates to several inventions or groups of inventions, namely:							
see sheet B							
All further search fees have been paid within the fixed time limit. The present European search report has been drawn up for all claims.							
As all searchable claims could be searched without effort justifying an additional fee, the Search Division did not invite payment of any additional fee.							
Only part of the further search fees have been paid within the fixed time limit. The present European search report has been drawn up for those parts of the European patent application which relate to the inventions in respect of which search fees have been paid, namely claims:							
None of the further search fees have been paid within the fixed time limit. The present European search report has been drawn up for those parts of the European patent application which relate to the invention first mentioned in the claims, namely claims:							



## LACK OF UNITY OF INVENTION SHEET B

Application Number

EP 01 31 0427

The Search Division considers that the present European patent application does not comply with the requirements of unity of invention and relates to several inventions or groups of inventions, namely:

1. Claims: claims 1-8

A bubble-jet printhead comprising a substrate with a manifold, an ink chamber and an ink channel, a nozzle plate, an annular heater, an electrode, and an adiabatic layer formed on the heater.

2. Claims: claims 9-18

A method of manufacturing a bubble-jet printhead, the method comprising the steps of: forming a nozzle plate on a surface of a substrate, forming a heater having an annular shape on the nozzle plate, etching a bottom side of the substrate and forming a manifold for supplying ink, forming an electrode, etching the nozzle plate and forming a nozzle, forming an adiabatic layer on the heater in the shape of an annulus, etching the substrate and forming an ink chamber, and etching the substrate and forming an ink channel.

3. Claims: claims 19-31

A bubble-jet printhead formed on a silicon-on-insulator wafer having a first substrate, an oxide layer and a second substrate, the bubble-jet printhead comprising a manifold, an ink chamber having a substantially hemispherical shape, a nozzle, an adiabatic barrier, an electrode, and a heater protective layer; and a method of manufacturing this bubble-jet printhead.

### ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO.

EP 01 31 0427

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on .

The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

15-01-2003

	nt documen search rep		Publication date		Patent family member(s)		Publication date
US 6019	<u> 457</u>	Α	01-02-2000	AT	136500	T	15-04-1996
02 0013	457	^	01-05-5000	AT		T	15-12-1996
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				AU	9000191		
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				DE		<u>D1</u>	05-12-199
				DE		T2	28-05-199
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				DE		T2	05-06-199
				EP	0498291		12-08-199
				EP	0498292		12-08-199
				EP	0498293	—	12-08-199
				JР	3015573		06-03-200
				JР		Α	15-02-199
				JP	3179545	<b>B2</b>	25-06-200
				JP	5338171	Α	21-12-199
			•	JP	3179546	B2	25 <b>-</b> 06-200
				JP	5338172	Α	21-12-199
				US	5815173	Α	29-09-199
				US	5841452	Α	24-11-199
			•	AU	676133	<b>B2</b>	06-03-199
				AU	65792 <del>9</del>	<b>B2</b>	30-03-199
			•	AU	667295	B2	21-03-199
				JP	5338178		21-12-199
US 586	1902	Α	19-01-1999	NONE			
WO 963	<b></b>	Α	17-10-1996	EP	0765234	A1	02-04-199
		••	<del> </del>	JP	10501772		17-02-199
			·	WO	9632274	A1	17-10-199
		•		US	5905517	A	18-05-199
							. *

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82